

NOTE

Diffusion of Water along "Closed" Mica Interfaces

The responses of internal cracks at recontacted mica interfaces to changes in external humidity are reported and analyzed. Cracks on interfaces reformed in lattice registry remain effectively stationary; cracks formed at interfaces with a twist misorientation expand and contract reversibly with increasing and decreasing humidity. The results indicate that the internal cracks in the misoriented configuration are accessible to atmospheric water, which diffuses along the dilated interface and lowers the interface energy, but remain impervious to other constituent molecules of air. © 1993 Academic Press, Inc.

The special behavior of liquids in confined geometries is of considerable fundamental interest to colloid scientists who study the effects of interfaces, geometrical confinement, and reduced dimensionality, and of practical interest to geologists and materials scientists in areas like brittle fracture, boundary lubrication, grain boundary diffusion, intercalation, permeation, pressure dissolution, and liquid-phase sintering. In recent years this special behavior has been studied using various experimental approaches, including direct intersurface force measurement, atomic force microscopy, and surface-sensitive spectroscopy. Additionally, computer simulations have been carried out to explore the structure and dynamics of molecules in thin films.

In the present paper we report and analyze some experimental observations in naturally occurring muscovite mica, demonstrating the sensitivity of interfacial liquid transport to intersurface geometrical constraints. We present evidence that water diffuses readily along an adhering interface formed between two atomically smooth but misoriented mica sheets. If the twist angle is zero, i.e., if the opposing surfaces are in "lattice registry," the water diffusion is reduced effectively to zero, consistent with the well known absence of water intercalation in muscovite mica. We also show that the other constituent molecules of air do not diffuse along these same interfaces, in either the oriented or misoriented configuration.

Specifically, our experiments involve measuring variations in the size of residual penny-like "lenticular" cracks at the interface between two adhering thin sheets of muscovite mica. Mica is an ideal material for such studies, because it can be cleaved along a crystal plane with atomic smoothness over large areas, and then "healed" by allowing the two freshly cleaved halves to reseat in adhesive contact (1–3). In the present case, specimen interfaces were formed by cleaving a mica sheet, $\approx 50 \mu\text{m}$ thick, in air at room temperature and ambient relative humidity of ≈ 0.4 ($\approx 40\%$); the two halves of this sheet were mutually rotated through $\approx 45^\circ$ about a common surface normal prior to recontact. The resulting healed configuration resembles a high-angle twist grain boundary (4). A control specimen was prepared without completely cleaving the mica sheet, allowing the crack to retract and reform the interface in the original lattice registry, i.e., with effectively zero rotation or lateral translation. It has previously been shown, from fracture experiments on "open" cracks (3) and recontact adhesion experiments in a surface-forces apparatus (5), that the adhesion energy is considerably higher for the registered than for the *mis*registered configuration, but that the adhesion energy for the latter is nevertheless substantial, indicating that interfacial rebonding is very real.

During the course of the specimen preparation a few isolated fragments of mica from the edge of the specimen fell onto the newly cleaved faces, wedging open residual lenticular cracks at the subsequently closed interfaces. These trapped bubble cracks are rendered highly visible in reflected light by a distinctive axisymmetric Fizeau fringe pattern, from which the crack profile and thence the crack radius can be determined (6). Several such cracks formed in each of our specimens, with radii of 0.3–1.5 mm and center openings of 1–4 μm , distant 0.5–10 mm from an edge. Additionally, one of our test specimens contained a naturally occurring lenticular crack on a non-coplanar virgin plane parallel to the cleavage interface.

The impetus for our experiments came from casual observations of the crack response to changing external atmospheric conditions. The cracks in the misoriented specimens expanded, slowly over several hours, with increasing external humidity. This expansion was reversible; i.e., on restoring the original external humidity the cracks contracted. No such distinctive change in crack size was apparent in the zero-rotation specimen. It is established from previous "open-crack" experiments that the interface energy of mica is diminished by the presence of water in the immediate environment (2, 3), and from simple fracture mechanics considerations that the size of penny cracks in fixed-displacement loading is inversely dependent on this interface energy (see below) (6). We are therefore led to conclude from the present study that the mica cleavage interface, not susceptible to intercalation in its virgin state, is rendered permeable to water by misorientation of opposing cleavage surfaces.

Following these observations, a quantitative evaluation of the bubble-crack response to controlled environmental changes was made. For this purpose, the specimens were enclosed within a specimen chamber seated on the stage of an optical microscope. Initially, the chamber was filled with saturated water vapor, and resealed for a period of several days (relative humidity 1.0). The chamber was then reopened, a desiccant (P_2O_5) placed within, and the chamber resealed for another several days. In this latter half-cycle, a "drying out" period of some hours ensued before the atmosphere achieved its final steady state (relative humidity <0.1). One of the misoriented specimens was subjected to a repeat cycle. Crack sizes were monitored continually via the Fizeau fringe patterns, in monochromatic light, to determine the time variation of crack radius. Individual evaluations of the crack radius could be made to better than $\pm 2\%$ in this way.

Results from observations on a selection of cracks in the misoriented specimens are plotted as the data points in Figs. 1 and 2. Figure 1b includes comparative data for the oriented specimen. After an initial lag time (≈ 1 ks, not apparent on the scales of Figs. 1 and 2), the cracks in the misoriented specimens expand over time in the saturated atmosphere, at first rapidly and then more slowly, ultimately asymptoting toward upper limiting values. In general, cracks closer to the specimen edge grow more rapidly than those further away. On reducing the humidity within the chamber, the cracks contract again, ultimately shrinking below their original sizes at ambient humidity; in this half-cycle a lag (drying out) time is now distinctly evident. Repeat cycles, as shown in Fig. 2, confirm the reversibility of the moisture effect. The total variation in crack radius is $\approx 10\%$ in Figs. 1a and 2. The healed cracks in the oriented specimen show no reversibility with environmental change, although the data in Fig. 1b do exhibit a monotonic drift of $\approx 2\%$ in radius over the duration of the experiment. The virgin crack referred to earlier showed no drift at all, within an experimental uncertainty of $\approx 1\%$, over several months of observation.

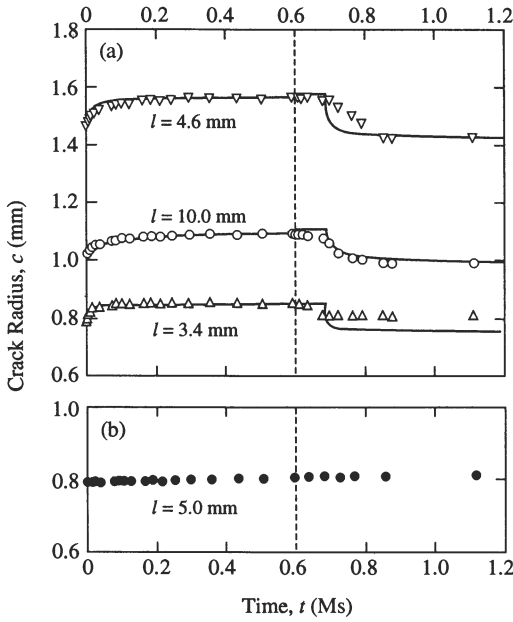


FIG. 1. Radius of lenticular cracks in mica as a function of time after external humidity changes. Crack distances l from specimen edge indicated. (a) Recontacted misoriented specimen. Solid curves are theoretical fits to data points, with adjusted interface energies: first interval ($t = 0$ to 0.59 Ms), $W_i = 180 \text{ J} \cdot \text{m}^{-2}$ ($\mathcal{R}_i = 0.4$) and $W_f = 125 \text{ J} \cdot \text{m}^{-2}$ ($\mathcal{R}_f = 1.0$); second interval ($t = 0.59$ to 1.11 Ms), $W_i = 125 \text{ J} \cdot \text{m}^{-2}$ ($\mathcal{R}_i = 1.0$) and $W_f = 200 \text{ J} \cdot \text{m}^{-2}$ ($\mathcal{R}_f = 0.1$), with incubation time 0.085 Ms. Adjusted diffusion coefficient $D = 2.6 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$. (b) Recontacted oriented specimen.

To quantify the kinetics of the intimated diffusion of water along the misoriented interfaces, we propose the following model. We begin with an explicit fracture mechanics relation for the crack radius c in terms of the reversible work W to separate the crack walls in the presence of the local environment within the bubble (i.e., the Dupré work of adhesion, or interface energy) (6):

$$c(W) = (16E'd^3W/3p^2)^{1/4} [1 - (1 - hp/W)^{1/2}]^{1/2}, \quad [1]$$

where d is an averaged thickness of the two mica sheets (6), $2h$ is the height of the internal wedging particle, p is the excess pressure within the bubble (relative to the external atmosphere), and $E' = E/(1 - \nu^2)$ with E Young's modulus and ν Poisson's ratio for mica.

The square bracket term in Eq. [1] allows for a buildup of internal pressure within the crack "bubble" during interfacial closure. Without due allowance for $p \neq 0$, the measured crack sizes for any given equilibrated interface at any given humidity are not mutually consistent with a single, well-defined value of W , e.g., as measured on open cracks (3). Evaluations of p for our cracks indicate many examples of internal pressures well in excess of 0.10 MPa (1 atm). Actually, p must vary with crack volume expansion and contraction during the course of our experiment. On the other hand, the cracks are reversible, so after a complete cycle p must revert to its original value. This value is found to remain constant thereafter at ambient humidity over periods exceeding 1 year (32 Ms). This implies that water is the only significantly mobile species at the misoriented mica interface; and, since the partial pressure of water is negligible compared to atmospheric pressures, this in turn suggests that the total number of trapped air molecules may be regarded as a time-invariant quantity for each crack. Accordingly, in Eq. [1] we allow for the p variation by computing the internal gas volume (from

integration over the crack profile) and requiring the internal pressure to satisfy the ideal gas law, at constant number of internal molecules and constant external pressure 0.10 MPa (6).

To model the variation of W with time, water is presumed to be present in a semi-infinite planar interface $x \geq 0$, x the distance from the specimen edge, initially in equilibrium with an external atmosphere at relative humidity \mathcal{R}_i . At time $t = 0$ the external humidity is abruptly changed to \mathcal{R}_f . The concentration $\mathcal{R}(x, t)$ of water in the interface at any subsequent instant then follows the familiar diffusion equation (7),

$$\mathcal{R}(x, t) = \mathcal{R}_i + (\mathcal{R}_f - \mathcal{R}_i) \text{erfc}[x/(4Dt)^{1/2}], \quad [2]$$

where erfc is the complementary error function and D is the diffusivity of water along the interface.

Consider a penny-shaped crack of radius c with center at $x = l$ from the specimen edge. In the limit $c \ll l$ the crack may be approximated as a point probe, sensitive to the local concentration but not perturbing it. This approximation is not particularly good in the present experiment (recall $c = 0.3$ –1 mm, $l = 0.5$ –10 mm). We nevertheless use it here because it captures the essential physics of the problem and simplifies the mathematics. The humidity within the crack is assumed to equilibrate with the local concentration in the interface. Within the variability of (independent, open-crack) experimental data (3, 8), the interface energy function $W(\mathcal{R})$ decreases linearly with relative humidity, so we may write directly from Eq. 2,

$$W(l, t) = W_i + (W_f - W_i) \text{erfc}[l/(4Dt)^{1/2}], \quad [3]$$

where W_i and W_f are the interface energies corresponding to the initial and final humidities. Equations [1] and [3] may then be solved simultaneously for $c(t)$ at any specified l .

The solid curves in Figs. 1 and 2 are appropriate data fits for the misoriented interfaces, with the following parametric adjustments (see the figure legends):

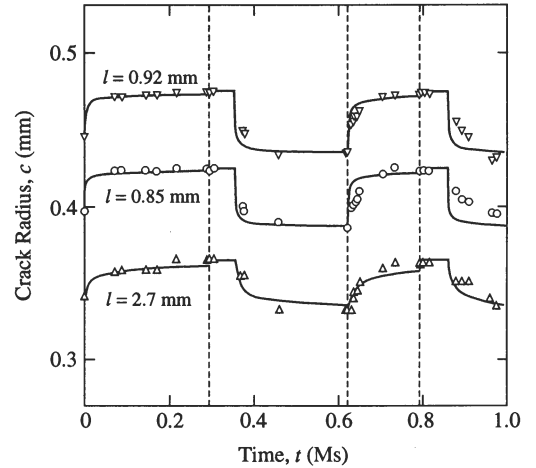


FIG. 2. Radius of lenticular cracks in mica as function of time after external humidity changes, for a second recontacted misoriented specimen. Crack distances l from specimen edge indicated. Solid curves are theoretical fits to data points, with adjusted interface energies: first interval ($t = 0$ to 0.29 Ms), $W_i = 180 \text{ J} \cdot \text{m}^{-2}$ ($\mathcal{R}_i = 0.4$) and $W_f = 138 \text{ J} \cdot \text{m}^{-2}$ ($\mathcal{R}_f = 1.0$); second interval ($t = 0.29$ to 0.62 Ms), $W_i = 138 \text{ J} \cdot \text{m}^{-2}$ ($\mathcal{R}_i = 1.0$) and $W_f = 200 \text{ J} \cdot \text{m}^{-2}$ ($\mathcal{R}_f = 0.1$), incubation time 0.065 Ms; third interval ($t = 0.62$ to 0.79 Ms), $W_i = 200 \text{ J} \cdot \text{m}^{-2}$ ($\mathcal{R}_i = 0.1$) and $W_f = 138 \text{ J} \cdot \text{m}^{-2}$ ($\mathcal{R}_f = 1.0$); fourth interval ($t = 0.79$ to 1.0 Ms), $W_i = 138 \text{ J} \cdot \text{m}^{-2}$ ($\mathcal{R}_i = 1.0$) and $W_f = 200 \text{ J} \cdot \text{m}^{-2}$ ($\mathcal{R}_f = 0.1$), incubation time 0.065 Ms. Adjusted diffusion coefficient $D = 4.0 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$.

interface energies W_i and W_f for all cracks in each specimen over each portion of the experimental cycle; diffusion coefficient D for all cracks in each specimen over the complete humidifying/drying cycle; for the drying half-cycles an "incubation" time, the same for all cracks in each specimen, to allow for the slow absorption of residual moisture within the chamber. The decline in interface energy over the full humidity range, $W \approx 200 \text{ mJ} \cdot \text{m}^{-2}$ at $R \approx 0.1$ to $W \approx 130 \text{ mJ} \cdot \text{m}^{-2}$ at $R \approx 1.0$, lies within the documented data range for open cracks (3, 8). The value $D \approx 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ is higher than any bulk diffusion coefficient for ionic-covalent solids at room temperature, and is more typical of surface or grain boundary diffusion coefficients (9).

We see that the model reproduces the main features of the rate-dependent, reversible crack evolution in the misoriented interfaces with change in external humidity. The fits are not ideal, presumably because of the oversimplification of the model, which omits consideration of the following features: geometrical perturbations, from the finite sizes of the lenticular cracks and the specimens, and unequal thicknesses of the mica cleavage halves; pressure dependence of relative humidity on varying internal pressure within the cracks; possible spatial variations in initial water concentration at the interface (especially on reversing the humidifying/drying cycle), as well as in local values of interface energy and diffusion coefficient. Nonetheless, the semi-quantitative agreement allows us at least to establish a first estimate of the diffusion coefficient of water along the misoriented mica-mica interfaces.

Earlier we mentioned how the inferred existence of an excess of gas pressure within the closed cracks may be taken as evidence for preferential diffusion of water molecules along the misoriented mica-mica interfaces. Apparently, the nitrogen and oxygen molecules in the air are too large to be accommodated within the interfacial interstices. Now, in virgin mica, cleavage occurs between symmetric layers of hexagonal oxygen rings (interplanar spacing 0.34 nm) with intervening recessed potassium ions (diameter 0.27 nm) (8, 10–12). If one were to separate and rotate the layers, then on recontact very few of the potassiums would be able to recess back into the oxygen-ring hollows on both sides; instead, some of those potassiums would align directly above oxygen centers, leaving the interface in a state of residual dilation (oxygen interplanar spacing 0.50 nm) (12). This dilation would be exacerbated by any occluded adsorbates (11, 12). From simple geometrical considerations of the mica structure, such a dilated interface would just be able to accommodate water molecules (diameter 0.28 nm) at interstitial sites between the potassiums (12). Molecules of oxygen (long dimension 0.41 nm) and nitrogen (long dimension 0.44 nm), on the other hand, would require substantially greater interfacial dilations. In this context, we may note that gas permeability rates through open silicate glass networks are at least six orders of magnitude smaller for nitrogen and oxygen than for water (or hydroxyls) (13).

The results presented here demonstrate the sensitivity of diffusion processes to departures from lattice registry at recontacted interfaces. Implications concerning the basic mechanisms of preferred molecular transport and ensuing decohesion at intersurface contacts, at grain and interphase boundaries in polycrystalline minerals and ceramics, and at fracture interfaces in brittle solids, are apparent. One may envisage the use of such interfaces as "molecular sieves." The occurrence of moisture-filled internal cracks can also result in anomalously large thermal expansion coefficients, as has been demonstrated in virgin phlogopite micas (14), raising the prospect of applications as thermal actuators (15).

ACKNOWLEDGMENTS

The authors are grateful to D. T. Smith for discussions on aspects of this study and to N. P. Padture for comments on the manuscript. Funding for this project was provided by the U.S. Office of Naval Research.

REFERENCES

1. Obreimoff, J. W., *Proc. R. Soc. London A* **127**, 290 (1930).
2. Bailey, A. I., and Kay, S. M., *Proc. R. Soc. London A* **301**, 47 (1967).
3. Wan, K-T., and Lawn, B. R., *Acta Metall.* **38**, 2073 (1990).
4. Lawn, B. R., Hockey, B. J., and Wiederhorn, S. M., *J. Mater. Sci.* **15**, 1207 (1980).
5. McGuiggan, P. M., and Israelachvili, J. N., *J. Mater. Res.* **5**, 2232 (1990).
6. Wan, K-T., Horn, R. G., Courmont, S., and Lawn, B. R., *J. Mater. Res.* **8**, 1128 (1993).
7. Crank, J., "The Mathematics of Diffusion." Oxford Univ. Press, Oxford, 1975.
8. Wan, K-T., Smith, D. T., and Lawn, B. R., *J. Am. Ceram. Soc.* **75**, 667 (1992).
9. Kingery, W. D., Bowen, H. K., and Uhlmann, D. R., "Introduction to Ceramics," Chap. 6. Wiley-Interscience, New York, 1976.
10. Bragg, W. L., and Claringbull, G. F., "Crystal Structures of Minerals," Vol. 4. Bell, London, 1965.
11. Bailey, A. I., *J. Appl. Phys.* **32**, 1407 (1961).
12. Lawn, B. R., Roach, D. H., and Thomson, R. M., *J. Mater. Sci.* **22**, 4036 (1987).
13. Holland, L., "The Properties of Glass Surfaces," Chap. 4, Wiley, New York, 1964.
14. Cartz, L., and Tooper, B., *J. Appl. Phys.* **36**, 2783 (1965).
15. Cartz, L., Kariotis, F. G., and Yang, X., in "New Materials and Their Applications" (D. Holland, Ed.), Institute of Physics Conf. Ser. No. 111, p. 507. Institute of Physics, London, 1990.

R. G. HORN¹
K-T. WAN²
S. COURMONT³
B. R. LAWN⁴

Materials Science and Engineering Laboratory
National Institute of Standards and Technology
Gaithersburg, Maryland 20899

Received November 23, 1992

¹ Now at Schools of Applied Physics and Chemical Technology, University of South Australia, The Levels, Pooraka, S.A. 5095, Australia.

² Current address: Department of Physics and Astronomy, University of Maryland, College Park, MD 20742.

³ Work done while on leave from Ecole Supérieure de Physique et de Chimie Industrielles de la Ville de Paris, F-75231 Paris, France.

⁴ To whom correspondence should be addressed.